RMD-81/5

Chemical Composition and Mutagenicity of Clover Bar Landfill Leachates

Alberta

ENVIRONMENT

CHEMICAL COMPOSITION AND MUTAGENICITY OF CLOVER BAR LANDFILL LEACHATES

by

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ALBERTA ENVIRONMENT

RMD-81/5

January 1981

91-02978/

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This report may be cited as:

Baker, B.L., K.R. Parker, and E. Peake. 1981. Chemical composition and mutagenicity of Clover Bar landfill leachates. Prep. for the Research Management Division, Alberta Environment by Kananaskis Centre for Environmental Research, The University of Calgary. RMD-81/5. 45 pp.

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ABSTRACT

The purpose of this study was to obtain a characterization of organic components and to measure mutagenic activity in leachates from the Clover Bar sanitary landfill site. The approach was to use standard water quality methodology in conjunction with extraction, separation, and other accepted procedures in defining the organic and mutagenic character of these leachates. Total organic carbon (TOC) abundances varied from 40 to 16 000 mg/L across the landfill site with the greatest abundances in leachates from the older (eastern) areas of the site. This same pattern held true for the majority of organic parameters measured, including chemical oxygen demands (COD). The apparent trend is the manifestation of a time factor in which one cell of buried waste has been deposited for a longer period of time than a second cell. Because of this factor, the first cell has undergone greater degradation and is characterized by higher levels of organic compounds. The most abundant class of organic compounds identified were the organic acids accounting for 25% of the TOC in wells near the older edge of the site. These organic acids are known products of microbial activity reported in landfill leachates in Europe and the United States. Phenols in these leachates (ranging from 0.03 to 7.6 mg/L) are present at levels very much higher than the limit for acceptable surface water abundances and represent a very significant hazard if permitted to escape into surface or groundwater resources. Some of the phenolic compounds identified are on the United States Environmental Protection Agency's (EPA) list of priority pollutants. Polychlorinated biphenyls were also observed (in very low concentrations--0.08 µg/L in one sample). Carbohydrates were seen in the range 0.004 to 0.6 mg/L, with the highest levels in leachates characterized by high TOC. Polycyclic aromatic hydrocarbons were either absent or present in amounts less than 0.001 mg/L. The Ames test showed mutagenic activity in extracts of the leachates and in the effluent sample. The activity was not high, ranging from the equivalent of 0.4 µg/L in the effluent to 12.8 µg/L of benzo(a)pyrene

equivalent in No. 1 leachate. Mutagenic levels decreased across the landfill site with increasing TOC and organic acids. Four recommendations are made for a more adequate characterization of Alberta landfill leachates and a better understanding of processes occurring within landfill sites.

1. INTRODUCTION

Sanitary landfills, the most common waste disposal method used in the industrial world, present potentially serious environmental problems through the movement of hazardous material from the landfill site into groundwaters and surface waters. The problem is potentially more serious at sites where hazardous waste materials are emplaced in addition to regular municipal and industrial wastes. The Clover Bar sanitary landfill site in Edmonton is one such site.

The Clover Bar site is located in Section 28, Township 53, Range 23 West of the 4th Meridian--just east of the city of Edmonton--and is situated on a river terrace on the south bank of the North Saskatchewan River. In this area, alluvial deposits reach a thickness of 8 m with a lower layer of gravel. The gravel layer contains a substantial amount of groundwater which moves along the surface of the underlying bedrock and appears as springs at the river (Wardrop and Associates 1978). The landfill site intercepts this gravel layer. Waste material deposited in the site is principally municipal wastes with some industrial and hazardous wastes. Potentially hazardous liquid wastes make up about 3% of the total amount deposited (Wardrop and Associates 1978).

Potential problems arise in sanitary landfill sites due to processes that form a liquid accumulation called "leachate". Leachate generation occurs as a result of two concomitant processes that alter the character of the deposited waste material--snow and rain water percolation through the waste material, and degradation of organic substances in the waste by microbial action (Livermore et al. 1969; Chen and Bowerman 1974; Oleckno 1976; Baedecker and Back 1979; van Engers 1978). Leachate formation depends on factors such as type of waste material deposited, landfill conditions (temperature, pH, Eh, moisture, and age), characteristics of external water, and composition of the covering soils (Baedecker and Back 1979). Leachates differ from one landfill site to another, depending on the operating conditions of the landfill. In sites where hazardous and liquid waster are also deposited, the character of the leachate is also altered (Oleckno 1976).

When leachate has formed in sufficient quantity to migrate beyond the boundaries of the landfill site into groundwater aquifers or surface waters, it could pose a threat to human health and that of other living systems.

Indiscriminate and long-term emplacement of waste chemicals in makeshift dumps has created serious environmental problems (Pojasek 1979). The media has brought some of these to the attention of the public--the Love Canal (Niagara Falls, NY), Valley of the Drums (West Point, KY), Toone Chemical Dump (Toone, TN), Silresim (Lowell, MA). Other sites are literally "waiting their turn" to be brought to the public's attention (Pojasek 1979). The United States Environmental Protection Agency has allotted a "superfund" of 1.6 billion dollars to aid in the cleanup of these hazardous sites. In the United States, there are over 32 000 sites nationwide that contain significant amounts of hazardous wastes. As many as 2000 of them present public health hazards. Comparative data for Canada are not available and protective steps cannot be taken until such information is forthcoming. The above references apply to old, unused disposal sites in the United States. Canada has similar sites. The time is rapidly approaching when some disaster is going to strike from such sources in Canada. There is probably a little more lead time in Alberta. To address such situations adequately, we must become familiar with present procedures of landfill operation, characterization of leachates and other hazardous substances in landfills, processes that occur in landfills, and possible changes in each of these aspects of waste management that could be implemented. One specific concern of waste management that must be addressed is the nature of the leachates generated in the landfills.

The present study was undertaken to provide a characterization of organic components in leachates from one sanitary landfill site in Alberta. It was designed to measure some of the general organic parameters, such as total organic carbon (TOC) and tannins and lignins, and then to identify specific organic compounds and to measure mutagenicity as an indication of potential carcinogenic

components. The approach was to apply standard water quality methods as well as extraction and separation procedures developed in the laboratory at the Kananaskis Centre for Environmental Research, The University of Calgary for the measurement of specific organic compounds in aqueous systems.

2. OBJECTIVES AND TERMS OF REFERENCE

The purpose of the present study was threefold:

1. To determine a partial list of organic compounds leached from the Clover Bar sanitary landfill site in the Edmonton area;
2. To determine a range in mutagenic activity of leachate and effluent waters from this site; and
3. To recommend methodology for the assessment of specific organic compounds and mutagens (potential carcinogens) in a leachate.

The study area of the project represented only samples from the Clover Bar sanitary landfill site in the Edmonton area as supplied by Alberta Environment. Given seven samples of Clover Bar landfill leachate, a number of functions were to be performed as follows:

1. Measure TOC, COD, tannins and lignins, phenols, and other such groups of compounds as may be readily analyzed colorimetrically;
2. Measure sulphur compounds, chlorinated hydrocarbons, alkane hydrocarbons, polycyclic aromatic hydrocarbons, and any such compounds that may be readily analyzed by gas chromatography;
3. Quantify the above so as to determine sample composition and variation amongst samples;
4. Carry out Ames tests on organic extracts of the water to detect mutagens (potential carcinogens) and to report mutagenic potencies of these extracts where possible;
5. Prepare a report on the findings of the research project, making recommendations concerning analytical methodology for determination of organic compounds in and mutagenicity of landfill leachates, and for further research;
6. Cooperate with James F. MacLaren Limited staff who are engaged in a parallel study; and
7. For B.L. Baker to attend Environmental Monitoring of Waste Disposal Operations conference in Arlington, VA., 29 and 30 October 1979 and submit a separate report on the conference.

3. SAMPLES AND WELL DESCRIPTIONS

A series of new wells was installed in the Clover Bar site by Alberta Environment to obtain samples for this study (Figure 1). The wells varied in depth from 55 to 80 ft, reaching into sandstone bedrock except in one case where the well reached mixed clay and grey-green sandstone. The total length of each well was cased with 2 in. diameter PVC with an 18 in. screen on the bottom of the casing.

Two series of samples were obtained--one in September 1979, the second in January 1980. Within this period, some samples taken from the same well differed in their physical appearance. At the time of the first sampling, no leachate was available in Well R-85-79 (sample No. 5), but in January, sufficient leachate was obtained for limited analyses. The initial objective was to study a set of samples from the Clover Bar site which were provided by Alberta Environment. These samples were received in September 1979. Sufficient sample was supplied from each well to conduct one series of analyses. A second set of leachate samples was obtained to extend the initial findings.

A water effluent sample was also obtained from a stream entering the North Saskatchewan River; this stream collects groundwaters and possibly some leachate from the perimeter of the landfill site.

Details of each well are shown in Table 1.

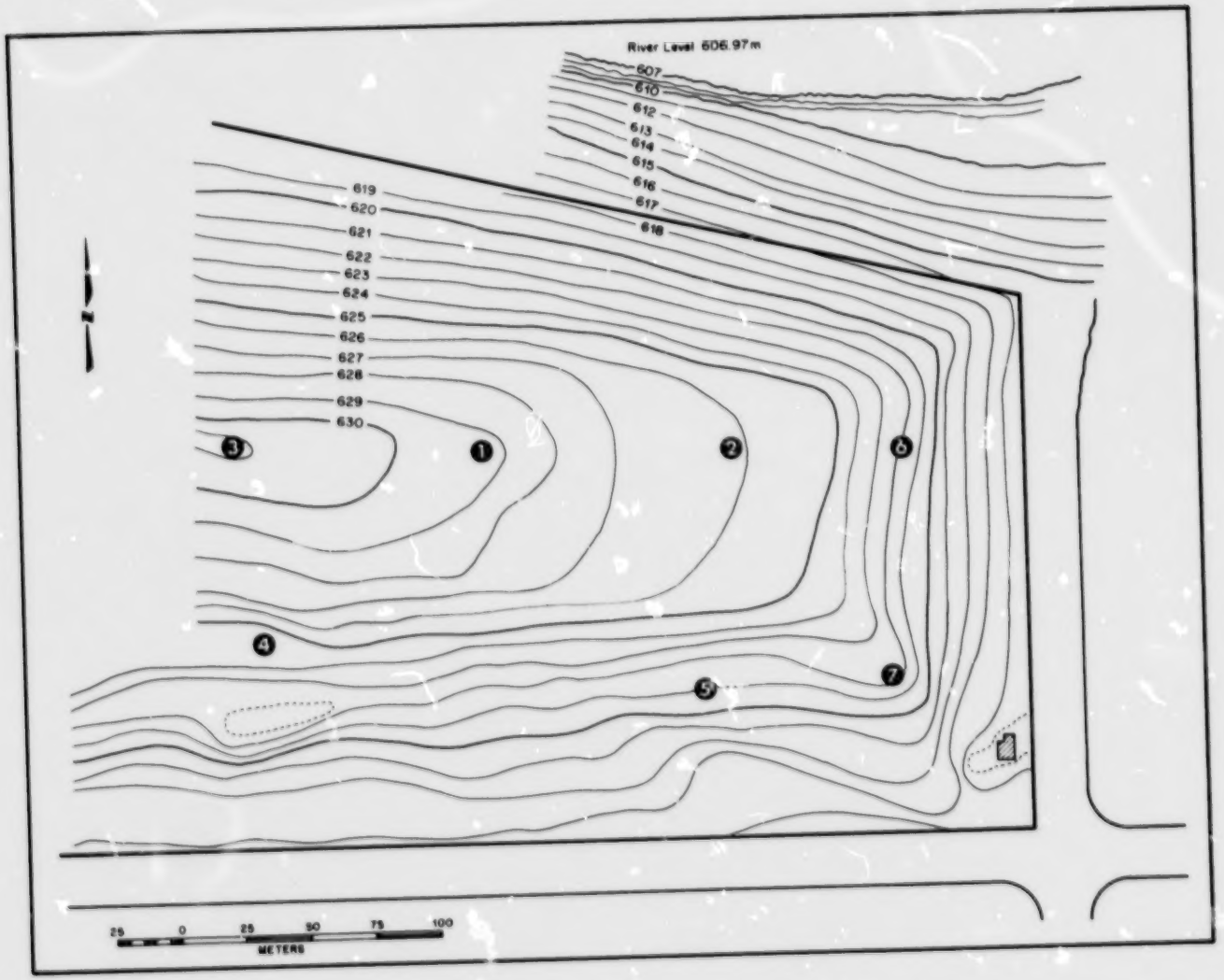

Figure 1. Location of sampled wells in the Clover Bar landfill site.

Table 1. Details of wells installed in the Clover Bar site.

Sample Number	Well	Depth (ft)	Texture and Lithology
1	R-77-79	0 - 3.5	Soil covering
		3.5 - 63	Refuse
		63 - 68	Sandstone and sand pooket
2	R-80-79	0 - 4	Soil covering
		4 - 63	Refuse
		63 - 80	Sandstone
3	R-81-79	0 - 4	Soil covering
		5.5 - 63	Refuse
		63 - 73	Mixed clay till
		73 - 80	Mixed clay till and grey-green sandstone
4	R-83-79	0 - 4	Soil covering
		4 - 49	Refuse
		49 - 55	Sandstone-mixed shale
5	R-85-79	0 - 6	Soil covering
		6 - 55	Refuse
		55 - 65	Sandstone - dry
6	R-86-79	0 - 6	Soil covering
		6 - 49	Refuse
		49 - 55	Sandstone
7	R-87-79	0 - 2.5	Soil covering
		2.5 - 54	Refuse
		54 - 57	Sandstone

4. METHODOLOGY

The analytical methods used in this study were adapted from those used for surface and wastewaters.

4.1 MEASUREMENT OF GENERAL PARAMETERS

Gross characterization of the leachates was carried out through measurements of pH, suspended solids, total organic carbon, chemical oxygen demand, phenols, tannins and lignins. Standard methods for analysis of these parameters, routinely used in the analysis of surface and wastewaters (American Public Health Association et al. 1971), were applied to this study. Such methods are not available for carbohydrates, suspended soilds, and total organic carbon. Hence, carbohydrates were measured according to the method of Antia and Lee (1963). Suspended solids were measured by filtering a measured volume of well-mixed leachate through a 0.45 μm millipore filter. The amount of sediment remaining on the filter was weighed after drying and related to the original volume of leachate. Total organic carbon was measured by direct injection of leachate into a Dohrmann D-52 total organic carbon analyzer (in most cases the leachate was diluted to ensure measurements in the operating range of the instrument).

4.2 ANALYSES OF SPECIFIC ORGANIC COMPOUNDS

Specific organic compounds cannot be determined directly in an aqueous medium. In most cases, their levels of occurrence in water are too low for direct measurement by present technology. To overcome this problem, the leachate was extracted with benzene according to ASTM method D 2778-70. The analytical procedure used initially in this study is shown in Figure 2. The pH of the leachate sample was adjusted to 2 for extraction with nanograde benzene to ensure complete extraction of neutral and acidic components. Subsequent treatment of the benzene extract with a 1% sodium hydroxide solution separated the acidic components from the neutral components. The acids and complex phenols were extracted into the aqueous layer while the neutral hydrocarbons remained in the organic benzene layer. The acidic components

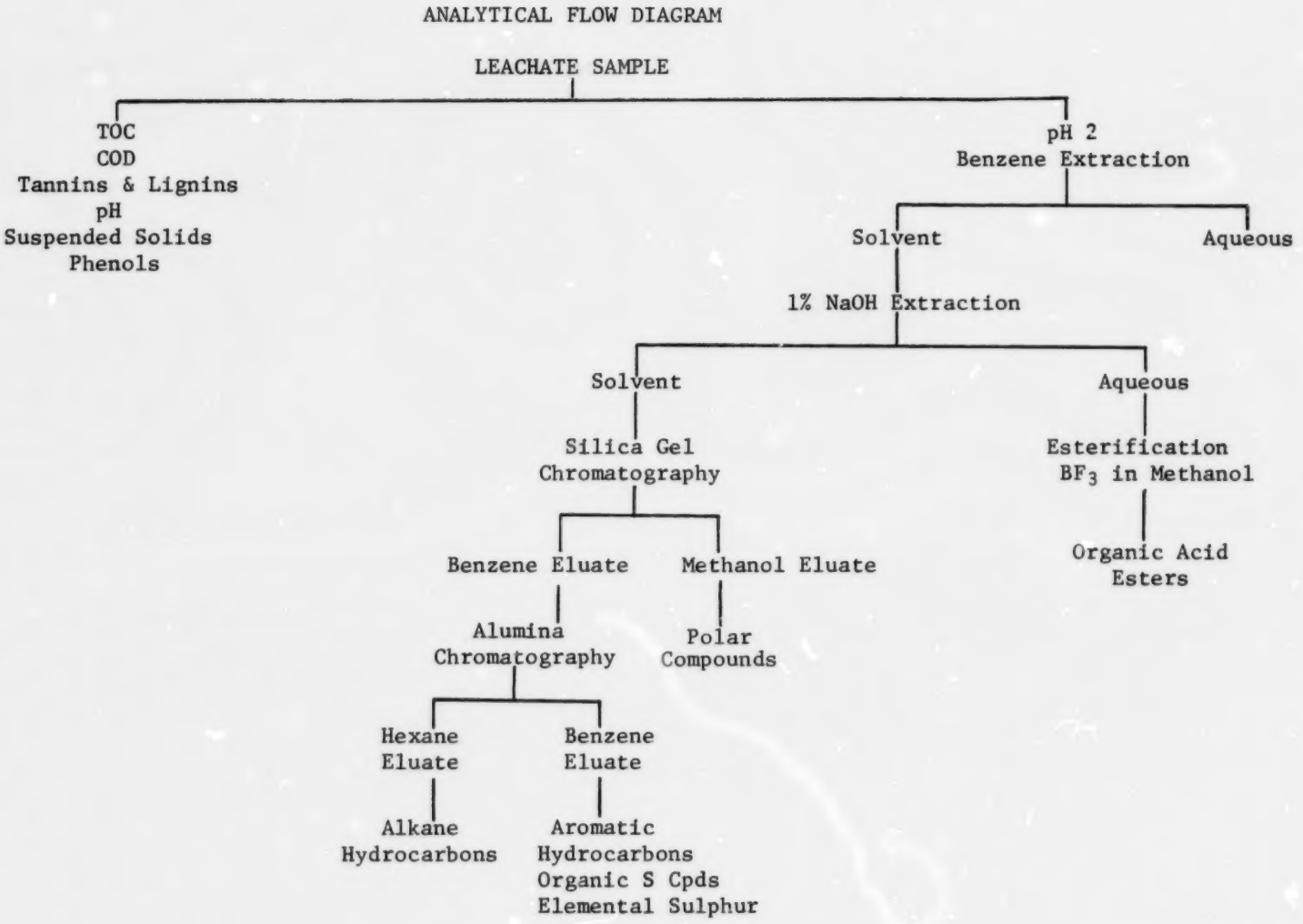

Figure 2. Analytical separation scheme for September samples.

(in the aqueous layer) were analyzed by gas chromatography. Since these components are too polar for easy passage through a chromatographic column, they were treated for analysis by esterification with boron trifluoride in methanol. Following esterification, the methyl esters of the organic acids were extracted from the aqueous esterification mixture with benzene and injected into the gas chromatograph. Identification and quantification of organic acids was made by comparison of retention times and responses of extracts with the corresponding data for standard solutions of organic acids. Confirmation of organic acid and complex phenol identifications was made using gas chromatography coupled with mass spectrometry. Here, identification is made by comparison of the fragmentation pattern of the compound in the sample with the very specific "finger print" fragmentation patterns of standard acids and phenols.

The neutral components, consisting of alkanes, aromatics, and polar compounds which remained in the benzene layer from the sodium hydroxide extraction, were separated into individual groups using column chromatography. Alkanes and aromatics were separated from polar compounds on a chromatographic column of silica gel. The alkane and aromatic fractions were eluted with benzene and the polar compounds with methanol. The polar compounds were transferred into either hexane or benzene for direct analysis by gas chromatography. The alkane and aromatic fractions were further separated on a chromatographic column containing activated alumina. The alkane hydrocarbons were eluted with hexane and the aromatic hydrocarbons with benzene. Included in the hexane eluate were elemental sulphur and organic sulphur compounds. Following elution from the alumina column, all of these compounds were analyzed by gas chromatography. The hydrocarbons were measured using flame ionization detection whereas the sulphur compounds were measured with a flame photometric detector.

In the first series of samples received in September, two problems arose: (1) polycyclic aromatic hydrocarbons were obscured by plasticizers; and (2) the highly acidic components extracted from leachates with high TOC levels were toxic to the bacteria used in the

Ames test. The separation procedure was altered for the second series (Figure 3). Extraction was carried out at a pH of 7.3 and aromatic hydrocarbons were measured directly (on extracts following removal of the acidic components with sodium hydroxide) on the GC/MS. The individual aromatic hydrocarbons were identified by comparison with standard aromatic hydrocarbon fragmentation patterns and retention characteristics.

Polychlorinated biphenyls (PCB's) were measured following extraction of the leachate, as received, with hexane. This extract was shaken with mercury to remove elemental sulphur then placed on a microchromatographic column of Florisil. The PCB's were eluted from this column with hexane, then detected and measured in a gas chromatograph fitted with an electron capture detector.

In this project, a total of 105 gas chromatographic analyses and 53 gas chromatograph-mass spectrometer (GC/MS) analyses were carried out covering both series of samples.

4.3 *SALMONELLA*/MAMMALIAN-MICROSOME MUTAGENICITY TEST (AMES TEST)

Extracts of the effluent and of Leachates 1 to 4 and 7 from the first series of samples, along with the effluent and Leachates 3, 4, 6, and 7 from the second series, were tested for mutagenic activity using the *Salmonella* mammalian-microsome mutagenicity test (Ames et al. 1973; McCann and Ames 1977). Samples from the second series were neutralized prior to benzene extraction to prevent inclusion of organic acids.

A portion of the benzene extract of the leachate sample was reduced to incipient dryness under $N_{2(g)}$. The residue was then weighed and dissolved in dimethylsulphoxide (DMSO) (200 to 500 µL). Extracts in DMSO were assayed for mutagenic activity using a quantitative plate test (Ames et al. 1973; McCann and Ames 1977) in which the sample, bacteria, and mammalian enzymes were incorporated in an overlay of molten agar on plates containing mineral glucose agar medium (1.5% Difco Bacto-agar, 0.2% glucose, 1.05% K_2HPO_4, 0.45% KH_2PO_4, 0.1% $(NH_4)_2SO_4$, and 0.01% $MgSO_4\ 7H_2O$).

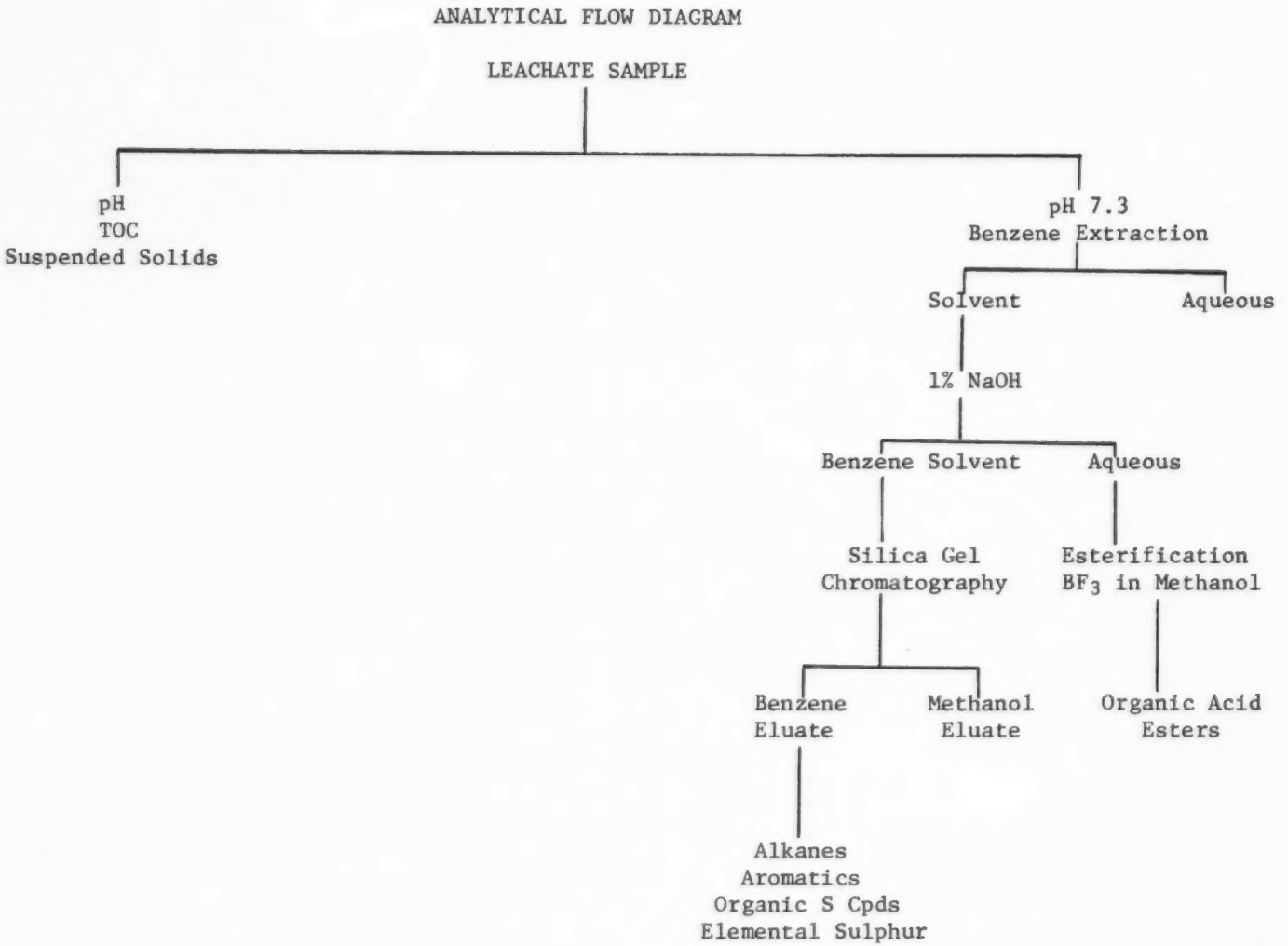

Figure 3. Analytical separation scheme for January samples.

Bacterial strains received from Dr. Bruce Ames, University of California (Berkeley), were checked for histidine requirement, deep rough character, ampicillin resistance, uv-sensitivity, and spontaneous reversion rate prior to storage as frozen cultures (-80°C). TA98 was the only strain used in the present study since it initially gave positive activity with the leachate samples. This strain detects frameshift mutations including those which are enhanced by the presence of an R-factor. The bacteria were grown overnight to saturation in a Penassay broth culture to which was added 0.1 mL of aqueous 0.2% ampicillin per 20 mL of broth. The use of ampicillin in the growth of strains which carry the R-factor (TA98 and TA100) inhibited the growth of cells which had lost the R-factor and so ensured a near 100% R^+ cell population in the saturated culture (Parker 1979).

Microsomal enzymes were obtained by homogenizing livers excised from rats injected 5 d previously with PCB (Aroclor 1254). Aliquots of the liver homogenate (termed S-9) were stored at -80°C until used. The optimum amount of S-9 per plate was determined with benzo(a)pyrene and sample extracts.

During routine testing, positive and negative controls were used to monitor consistency in both enzyme activity and bacterial properties.

The linear dose range was obtained by initially testing samples at a wide range of concentrations. Having determined the region of linearity (i.e., region of minimal toxicity), a narrower range of concentrations was used to determine the activity quantitatively. The slope of the line represents the mutagenic activity of the sample expressed in numbers of revertants per microlitre of DMSO. From this can be calculated the number of revertants per litre of water sample.

5. RESULTS AND DISCUSSION

5.1 TOTAL ORGANIC CARBON

A wide range was observed in TOC values in leachate samples from both series of samples. Wells giving leachates with high TOC levels in the first series of samples also gave leachates with elevated TOC levels in the second series. Leachate samples 2, 6, and 7 in Series I were characterized by TOC values which ranged from 7200 to 16 000 mg/L, whereas in Series II, ranged from 2600 to 11 000 mg/L. The remaining three leachates had significantly lower TOC values (in both series of samples) between 40 and 1500 mg/L (Table 2). Variation across the landfill site indicates microbial generation of organic compounds in older sections (i.e., Sites 2, 6, and 7) of the site. A TOC of 8 mg/L in both effluent samples was similar to normal values in surface waters (Baker et al. 1976).

The high TOC levels seen here are common in sanitary landfill leachates. Studies of landfills in California, the United Kingdom, and Norway (Johansen and Carlson 1976; Nerz 1954; British Ministry of Housing and Local government 1961) report levels from 100 to 7300 mg/L. These values are characteristic of initial stages of rapid anaerobic decomposition of organic waste material deposited in the landfill. These early decomposition processes result in generation of large quantities of complex water-soluble organic substances that are readily accommodated in the aqueous leachate.

5.2 SUSPENDED SOLIDS

Suspended solids varied widely from one leachate sample to another in both series (Table 2). Values ranged from 1 g/L to as high as 170 g/L. This variation directly reflects the amount of leachate available in each well. Wells with limited amounts of leachate had the greatest amounts of suspended solids.

Table 2. Organic constituents in Clover Bar leachates.

Sample	pH	Suspended Solids (g/L)	TOC (mg/L)	COD (mg/L)	Tannins & Lignins (mg/L)	Total Org. Acids (mg/L)	Org. S. Cpds. (µg/L)	Elemental Sulphur (µg/L)	Total Alkanes (µg/L)	Total Aromatics (µg/L)	Polar Compounds (µg/L)	Total Phenols (µg/L)	Carbo-Hydrates (µg/L)
Series I - Sampled September 1979													
1	-		1 500	5 100	3		90	2 800	4 100	-	400	60	4
2	6.4	2.1	11 000	25 900	170		3 000	<1	1 200	-	300	1 600	570
2A	6.9	170	12 700	30 500	410		5 100	<1	2 800	-	540	-	510
3	8.4	1.7	460	430	21		<10	20	2 100	-	260	30	15
4	-	-	300	290	15		120	220	6 500	-	370	30	-
6	5.8	4.6	16 100	29 800	2 200		9 700	<1	800	-	2 500	7 600	240
7	6.9	2.1	7 200	18 400	190		2 900	<1	250	-	500	2 250	90
EFF	8.1	<1.0	8	45	1		<10	<1	80	-	40	<1	<1
Series II - Sampled January 1980													
1	7.6	62.9	1 500	-	-	0.2	-	-	-	<1	-	-	-
2	6.3	1.8	11 100	-	-	3 000	-	-	-	<1	-	-	-
3	7.2	18.6	110	-	-	0.2	-	-	-	<1	-	-	-
4	7.5	1.1	40	-	-	0.1	-	-	-	<1	-	-	-
5	7.1	150	1 050	-	-	0.2	70	1 300	-	<1	-	-	-
6	6.4	3.3	6 800	-	-	700	-	60	-	<1	-	-	-
7	6.8	2.7	2 600	-	-	700	-	30	-	<1	-	-	-
EFF	7.2	<1.0	8	-	-	<0.1	-	<1	-	<1	-	-	-

5.3 CHEMICAL OXYGEN DEMAND

Chemical oxygen demand measurements were carried out only on the first series of samples. Levels, varying from 45 to 30 000 mg/L (Table 2), conform almost directly to the findings for TOC. High levels of organic compounds provide high oxygen demands as defined in the standard analytical method. The COD measured in the effluent differed little from that of surface waters and indicates insignificant direct contact between leachates and groundwater. Chemical oxygen demand on some occasions exceeded TOC values. This is attributed to interfering inorganic ions in the COD analyses.

5.4 TANNINS AND LIGNINS

Tannins and lignins represent the more stable organic compounds in aqueous systems. These refractory organic compounds also exhibited the west-to-east pattern of increasing levels observed for TOC and COD in the leachate samples. Data obtained for tannins and lignins show a range from 1 to 2200 mg/L (Table 2) which is about three orders of magnitude higher than in surface waters.

5.5 PHENOLS

Two different analytical techniques were used for the measurement of phenols in the landfill leachates. The standard colorimetric procedure was used to measure total phenolic content. Individual phenolic compounds were identified by gas chromatographic analyses coupled with mass spectrometry. The colorimetric test revealed very high levels of phenols in three of the seven samples. These high values were found in leachates containing high levels of other organic constituents, again reflecting the west-to-east increasing pattern noted earlier. The low levels observed in Leachates 1, 3, and 5 exceeded potable limits. Data for simple phenols ranged from 0.03 to 7.6 mg/L and are reported in Table 2. The phenol content of the effluent was low--less than 1 µg/L and comparable with river waters--indicating only limited contact of leachates with groundwater.

5.6 CARBOHYDRATES

In normal surface waters, the level of nutrients for microorganisms living in the water is often estimated through measurement of carbohydrates. This class of organic compounds was measured in the first series of leachate samples and the results of the tests are reported in Table 2. Normally in stream waters, carbohydrates are present at about 7 µg/L. In the highly organic leachates studied in this project, carbohydrates reached levels higher than 500 µg/L, but the effluent contained less than 1 µg/L. Again, levels of carbohydrates mirrored the west-to-east pattern where higher levels were noted in the eastern area of the landfill.

5.7 ALKANE HYDROCARBONS

The alkane hydrocarbons are very closely related to refined petroleum products. They are hydrophobic but do have a finite accommodation in aqueous systems. Analytical procedures were first developed for the investigation of these compounds in aqueous sytems as a significant part of geochemical studies concerning the origin and accumulation of petroleum. The pattern of abundances of total alkanes in fractions extracted from Clover Bar leachate samples does not follow the pattern observed for other organic constituents reported above. High levels of alkanes (2.1 to 6.5 mg/L) were found in leachates with relatively low levels of organic substances (Leachates 1, 3, and 4). Thus, leachate from wells in the newer section of the site may not have experienced microbial decomposition of alkane hydrocarbons. In contrast, other specific microbial decompositional processes may result in alkane generation. This was tested by determining the carbon preference index (CPI) of the n-alkanes in the leachates. The source of hydrocarbons can sometimes be distinguished on the basis of the CPI--the ratio of odd-numbered alkanes to even-numbered alkanes in the C_{21} to C_{35} range. The CPI of alkanes in extracted fractions from the Series I leachate samples showed values near unity (Table 3). If these alkanes had arisen from vegetation or soil, the CPI would have been three or more times higher, whereas bacteria and petroleum products

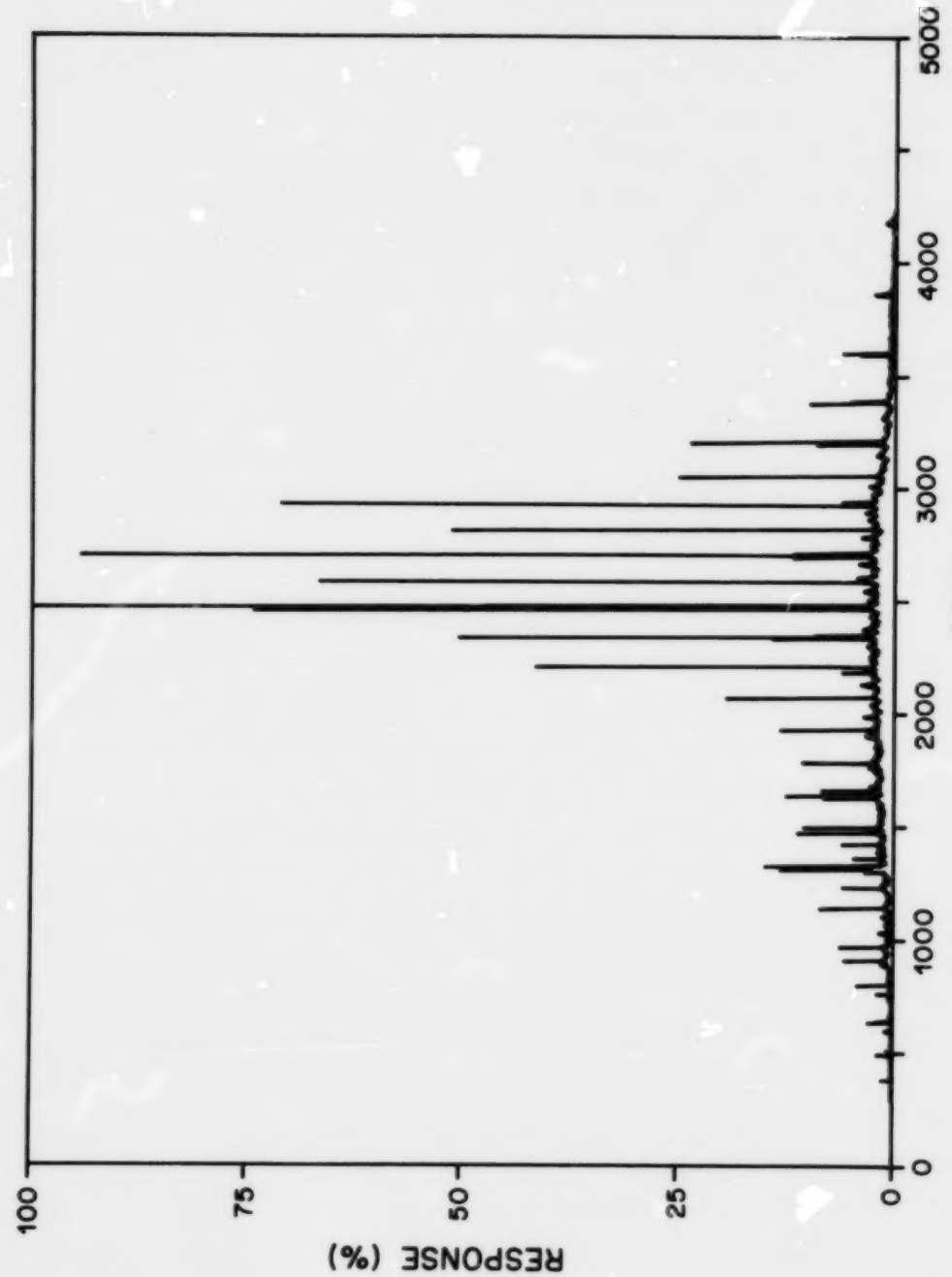

Figure 4. Distribution of n-alkanes in landfill Leachate 1.

Table 3. Distribution of alkane hydrocarbons in Clover Bar leachates leachates (µg/L).

Sample	1	2	3	4	6	7	EFF
Alkane							
C_{15}							1
C_{16}	7	2			4		1
C_{17}	8	3	2			3	1
C_{18}		4		4		1	1
C_{19}	16	3	2	9		1	1
C_{20}	6		3	4	1	2	1
C_{21}	9	40	3	45	2	2	1
C_{22}	20	140	5	9	5	1	1
C_{23}	40	75	9	9	6	1	1
C_{24}	45	100	13	13	9	2	1
C_{25}	90	115	27	16	12	3	1
C_{26}	80	130	40	15	15	4	1
C_{27}	130	125	50	30	12	5	1
C_{28}	105	110	50	25	25	3	1
C_{29}	150	90	75	55	40	12	1
C_{30}	95	60	50	35	18		1
C_{31}	115	5	50	40	17	3	1
C_{32}	65	50	50	25	11	2	1
C_{33}	65	45	50	30	12		
C_{34}	340	30	80	25	12		
C_{35}	35	25	70	35	5		1
C_{36}	17	20	65	40			
C_{37}			65	40			
C_{38}			65	26			
C_{39}			35	16			
C_{40}			22				
CPI (C_{16}-C_{35})	1.4	0.8	1.2	1.4	1.1	2.0	1.1
Major Alkane	C_{29}	C_{22}	C_{29}	C_{29}	C_{29}	C_{29}	C_{29}

show near-unity values. Since the leachates show values near unity, it appears that alkanes probably arose from oil dumped in the site or possible from microbiological generation within the landfill.

5.8 SULPHUR COMPOUNDS

The fraction containing alkanes also included sulphur and organic sulphur compounds. Detection of these compounds was by gas chromatography using a flame photometric detector. An interesting pattern emerged from these analyses in leachates. Leachates with high levels of organic substances were characterized by high amounts of organic sulphur compounds (3.0 to 9.7 mg/L) with no significant amounts of elemental sulphur. Leachates with low levels of organic compounds contained elemental sulphur with relatively small amounts of sulphur-containing organic compounds. The clear distinction between the occurrence of elemental sulphur and/or organic sulphur compounds in leachate extracts is seen in Figure 5 and 6. The gas chromatogram of organic sulphur compounds in a high TOC leachate is shown in Figure 5. If elemental sulphur were present in the leachate, another adsorption peak would appear to the right of the organic sulphur peaks at a temperature slightly above 230^{o}C. Figure 6 shows a reconstructed ion chromatograph taken from the mass spectrometer in which the single elemental sulphur peak is evident. Responses to the left of the elemental sulphur peak would indicate the presence of organic sulphur compounds. In the first series of samples, leachates with high levels of organic sulphur compounds were accompanied by little or no elemental sulphur. Where elemental sulphur was abundant, only small amounts of organic sulphur compounds were present.

The second series of samples displayed a different pattern in that elemental sulphur was somewhat more abundant. Leachates 6 and 7, which were characterized in the first series with high levels of organic sulphur compounds and no elemental sulphur, again had high organic sulphur. However, instead of having no elemental sulphur, they contained small but significant amounts of elemental sulphur.

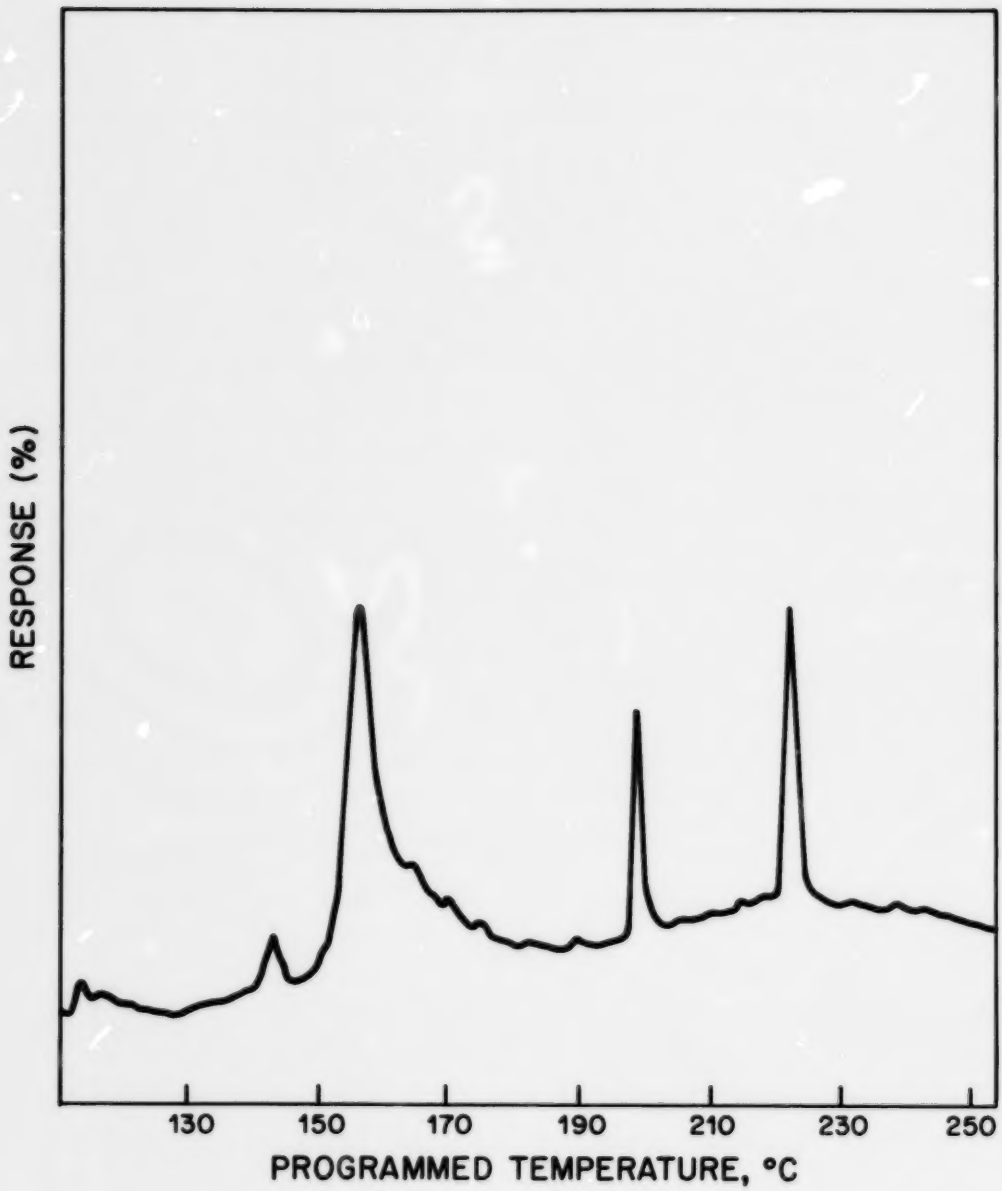

Figure 5. Gas chromatogram of organic sulphur compounds in leachates. Elemental sulphur is retained to temperatures higher than 200°C.

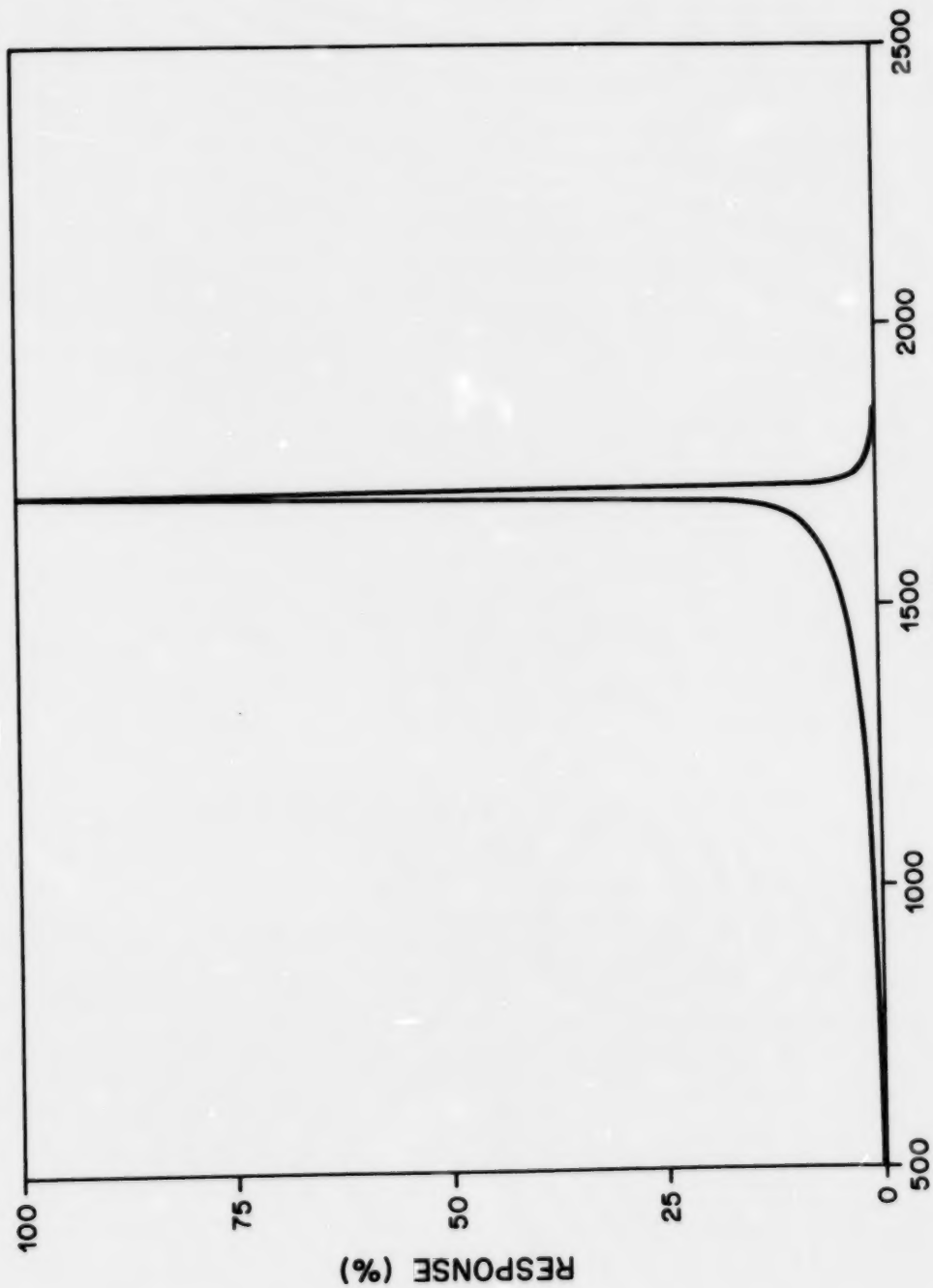

Figure 6. Gas chromatogram of elemental sulphur in landfill leachates.

These variations in leachate composition from one sampling time to another may indicate changes in decomposition processes or differences in the sampled material as outlined earlier. Further studies must be carried out to explain and define this varying behavior.

5.9 POLYCYCLIC AROMATIC HYDROCARBONS

Identification and quantitation of these hydrocarbons was not possible in the first series of samples due to complete obscuring of the aromatics by plasticizers. Partial quantification was possible using gas chromatography-mass spectrometry on the second series of samples. Analyses showed polycyclic aromatic hydrocarbons present in quantities less than 1 µg/L. The mutagenicity testing reported later is in accord with these low levels of aromatics.

5.10 POLAR COMPOUNDS

Polar compounds are defined as material eluted from a chromatographic column with methanol after elution of alkanes and aromatics with hexane and benzene. It is known that nitrogen-containing compounds are probably included in this group. Polar compounds in leachates ranged from 0.3 to 2.5 mg/L with 0.04 mg/L in the effluent (Table 2). The west-to-east pattern exhibited by other parameters was not evident in these fractions.

5.11 ORGANIC ACIDS

Organic acids have characteristically pungent odors that were abundantly apparent in both series of samples--especially in Leachates 2, 2A, 6, and 7. Identification and measurement of the organic acids in the Clover Bar leachates involved GC/MS analysis of their methyl esters. The higher volatility of esterified organic acids permitted their passage through gas chromatographic columns and subsequent detection by flame ionization. Unfortunately, losses of the lighter acids were encountered during analysis of the first series of samples--mainly in the esterification process. The second series of leachate samples was extracted and esterified under a revised experimental protocol that provided much more rigorous control over volatile acids,

permitting quantification of organic acids from butyric acid upward. Levels of total acids, ranging from 0.1 to more than 3000 mg/L were highest in leachate with high organic carbon content. In the effluent they were less than 0.1 mg/L. The west-to-east trend noted in other organic parameters was very noticeable, with high levels of organic acids found in the eastern part of the landfill.

The levels of organic acids are reflected in the pH values of the leachates. Leachates with high acid contents (and high levels of organic carbon) were slightly acidic, whereas leachates with low levels of organic acids had slightly alkaline pH levels (Table 2). The range of pH values was quite narrow--from 6.3 to 8.4. The high acid, low pH leachates are located in the eastward side of the landfill site; the low acid, higher pH leachates are on the west side of the site where most recent landfill operations were conducted. These observations reflect the increase in time available for anaerobic (fermentation) decomposition processes in the older part of the site to build up leachates abundant in organic acids.

The major acids identified in this study were butyric, pentanoic, and hexanoic acids (Table 4). Identification was based on fragmentation patterns of compounds responsible for chromatographic peaks obtained by GC/MS analysis. Fragmentation patterns for selected organic acids seen in the leachates along with those for standard organic acids are shown in Figures 7 to 9. Quantitation of individual acids showed variations from 0.003 to nearly 2000 mg/L (Table 5).

In Leachates 2, 6, and 7, organic acids accounted for about 25% of the total organic carbon. Other studies have shown that low molecular weight organic acids make up almost 90% of the organic carbon in "high strength" leachates (Johansen and Carlson 1976). In the Norwegian and American leachates with high levels of total organic carbon, the dominant acids were acetic, propionic, butyric, pentanoic, and hexanoic acids--acids with carbon chain lengths from two to six carbon atoms. The first three acids were most abundant. In the Clover Bar study, the very light organic acids (acetic and propionic) may have been hidden in the solvent peak of the gas

Table 4. Organic acids identified in Clover Bar leachates.

Leachate	Butyric	Pentanoic	Hexanoic	Cyclohexane Carboxylic	Heptanoic	Octanoic	Nonanoic	Decanoic	Benzene Acetic	Benzene Propionic
1			+[a]				+	Major		
2	+	Major	Major	+	+	+	+		+	+
3			+	Major	+	+	+	+	+	
4		+	Major	+	+	+		+		
5	+	+	Major	+	+	+	+	+		
6	+	Major	Major	+	+	+	+		+	+
7	+	+	Major	+	+	+	+		+	+
Effluent			+					Major		

[a] Indicates the organic acid was identified in significant quantities in the leachate.

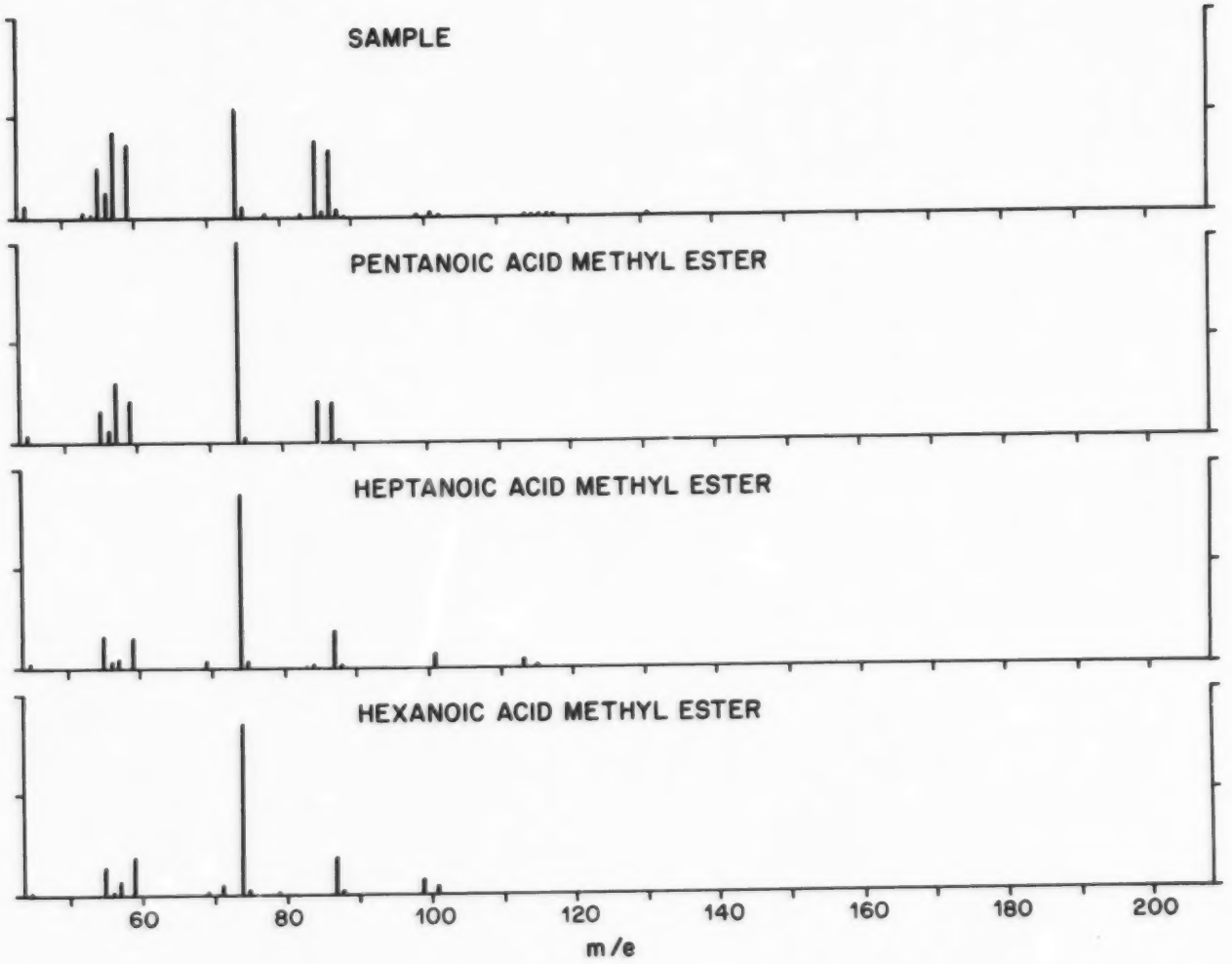

Figure 7. Fragmentation pattern of an organic acid identified in Leachate 5 compared with the patterns of pentanoic, heptanoic, and hexanoic acids.

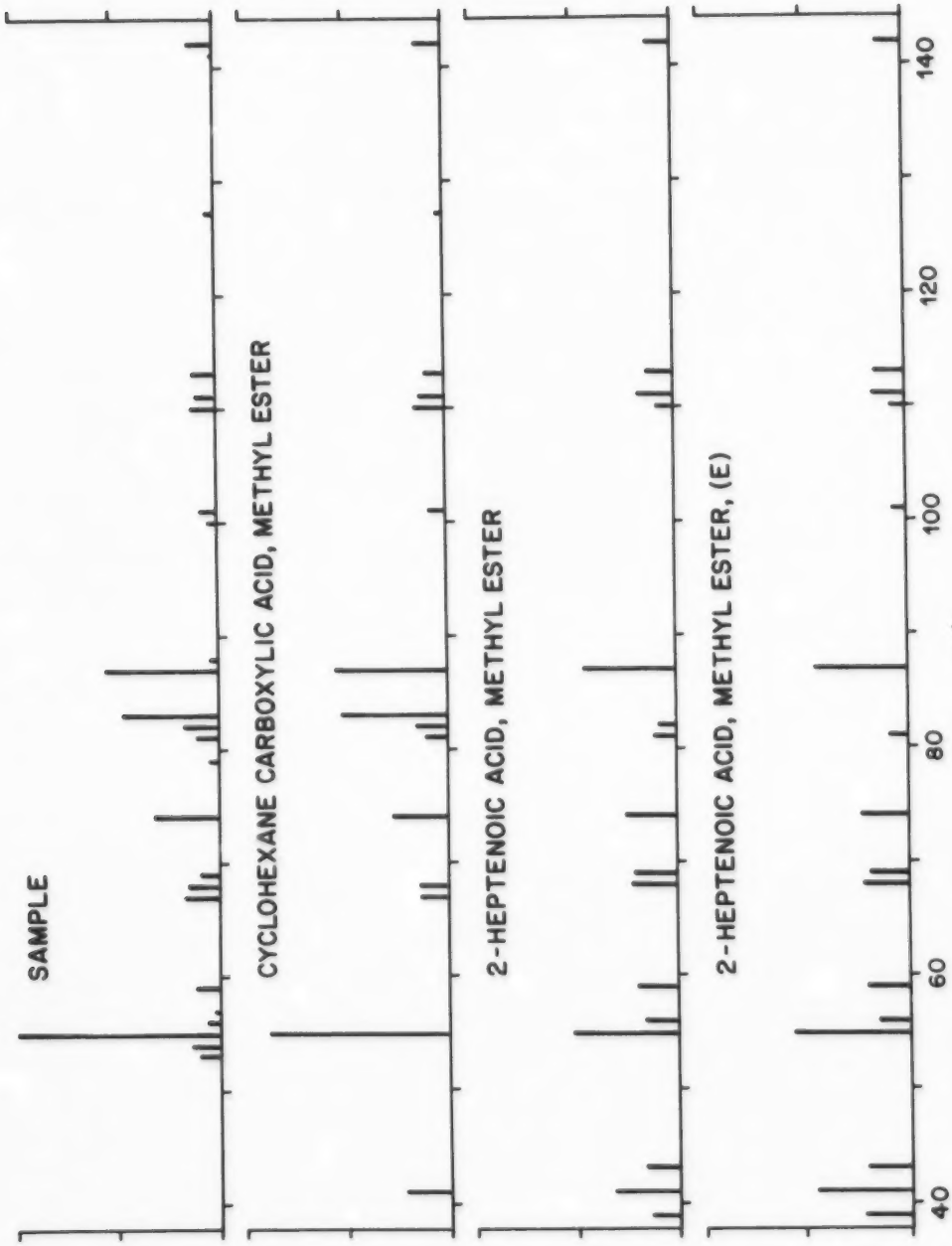

Figure 8. Fragmentation patterns of an organic acid identified in Leachate 6 compared with the pattern for cyclohexane carboxylic acid.

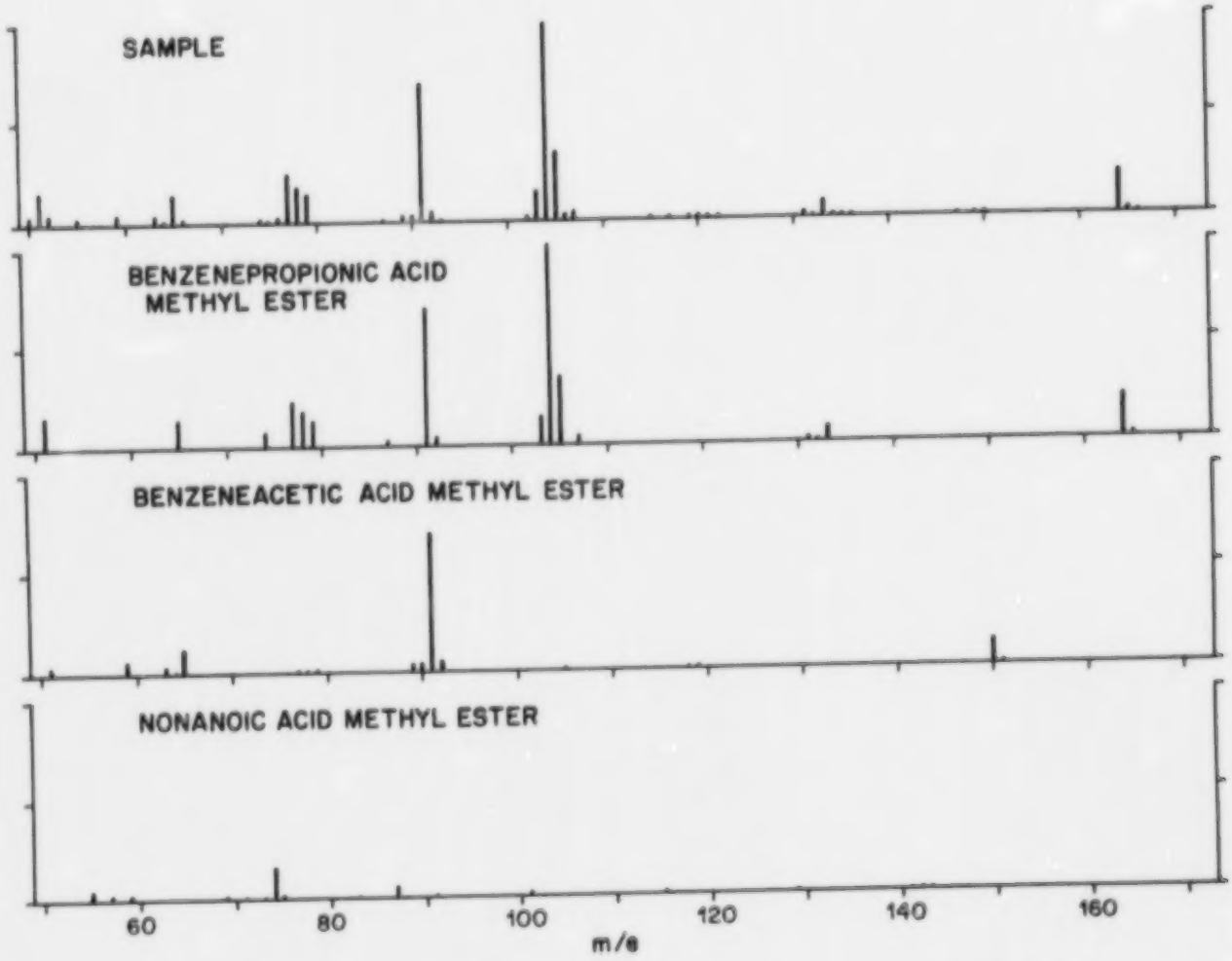

Figure 9. Fragmentation pattern of an organic acid identified with patterns of benzene propionic, benzene acetic, and nonanoic acids.

Table 5. Quantification of organic acids in Clover Bar leachates (µg/L).

Organic Acid	1	2	3	4	5	6	7	Eff
Unknown		175 000				38 300	7 100	
Unknown		88 500				9 200	11 600	
Butyric Acid	9	1 751 000			17	393 200	80 000	
Unknown		94 000				12 800	18 800	
Unknown		104 400				9 400	8 700	
Pentanoic Acid	13	275 000	3	3	19	69 600	111 700	
Unknown						2 500	16 300	
Hexanoic Acid	80	461 100	40	32	75	124 200	350 700	5
Unknown				3	5	2 000	11 700	
Cyclohexane-Carboxylic	20	35 200	90	9	12	10 100	8 300	
Heptanoic Acid	15		15	22	27	12 100	29 100	
Octanoic Acid	20		35	14	22	3 600	13 700	6
Unknown				8			3 000	
Phenyl Acetic Acid	7	16 700	3			4 800		
Nonanoic	8		8		4			
Hydrocinnamic Acid	16					9 900	8 900	1
Decanoic		31 300	30	41	28			2
TOTAL	188	3 029 200	224	132	209	701 700	679 500	14

chromatogram or were lost as highly volatile components. This could explain why organic acids in this study accounted for only 25% of carbon. Further studies to ensure identification and measurement of low weight organic acids must be conducted for a better definition of the position of organic acids in landfill leachate generation processes.

5.12 AMES TEST

Mutagenic data (strain TA98 with incorporation of S-9) are presented in Figure 10 and Tables 6, 7, and 8. Derivation of linear mutagenic activity is shown in Figure 10 for Leachate 4 (Series II) in which a potency of 0.150 revertants per microgram extract was obtained (reported in Table 8 as 150 rev./mg). Mutagenic activities or organic extracts (i.e., rev./µg extract) were determined in this manner for each sample by plotting the number of revertant colonies per plate against the dose (µg). The bacterial plate counts per test with extracts from Series I and II are given in Tables 6 and 7. Table 8 summarizes the mutagenic activities derived from linear plots of these data.

All of the leachate extracts tested indicated some mutagenic activity (Table 8). Total revertants per litre of water was calculated by multiplication of mutagenic activity per milligram of extract by the amount of extract (mg) per litre of water. These activities ranged from 120 (Leachate 7) to 1260 (Leachate 1) revertants per litre of water. Leachates 3 and 4 had approximately the same mutagenic activity (300 to 350 rev./L of water) and this estimate was consistent over two sampling times not-withstanding modification in the method of extraction of the two series. Leachates 6 and 7 contained light-weight carboxylic acids and these substances probably contributed to the observed toxicity of Series I extracts to the bacteria (e.g., activity of 0 reported in Table 8 for Leachate 7). Mutagenic activity was revealed in these extracts when the samples were neutralized with base to pH 7.0 which prevented uptake of carboxylic acids into benzene (i.e., Series II).

The effluent had very little mutagenic activity in September and January. An activity of 40 revertants per litre of effluent water for September was lower than the reported leachate activities.

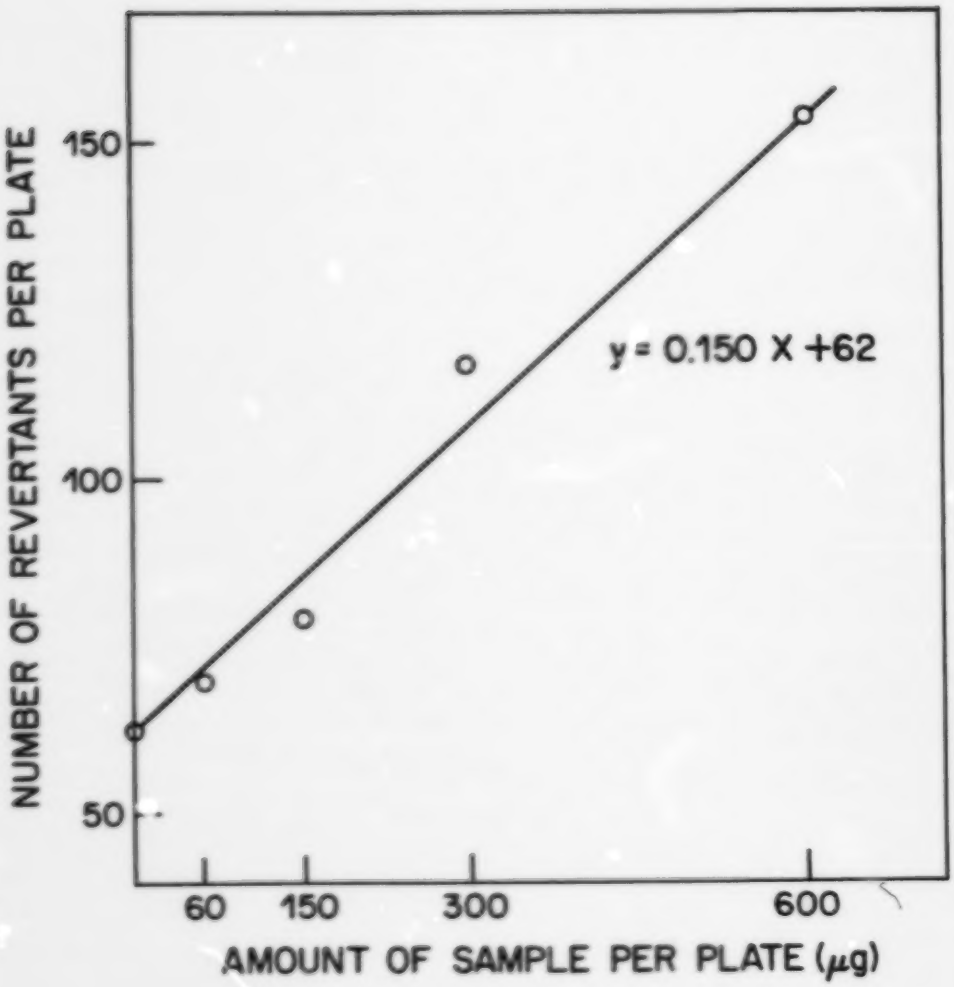

Figure 10. Dose-response activity on strain TA98 (with S-9) of extracts from leachate and effluent water samples. Represented here is landfill Leachate 4 (extraction Series II) with an activity of 150 revertants per mg sample.

Table 6. Revertant colonies per plate (strain TA98, plus S-9[a]) with extracted water samples: Series I[b].

Sample	DMSO Volume (mL)	Amount of Sample per Plate µg	Amount of Sample per Plate µL	Volume of Water Represented (mL)	No. of Revertants per Plate
1	5.2	6.1	5	0.19	41
		30.3	25	0.92	57
		121	100	3.70	40
	0.5	63	5	1.90	91
		315	25	9.60	102
		1260	100	38.5	136
3	0.2	55	5	10	66
		275	25	50	98
		1100	100	200	143
4	0.2	95	5	10	80
		475	25	50	115
		1900	100	200	147
Effluent	0.1	15	5	40	73
		60	20	160	67
		150	50	400	96
BaP	-	0.5	25	-	116
		1.0	25		179
		1.5	25		207
		2.0	25		310
DMSO	-	-	25	-	68 85
					45 76

[a] 50 µL per plate.

[b] benzene extracts of leachate and effluent water samples subsequently dissolved in DMSO for mutagenic testing.

Table 7. Revertant colonies per plate (strain TA98, plus S-9[a]) with extracted water samples: Series IIb.

Sample	DMSO Volume (mL)	Amount of Sample per Plate		Volume of Water Represented (mL)	No. of Revertants per Plate
		µg	µL		
3	0.2	65	10	25	59
		162	25	62.5	94
		325	50	125	79
		650	100	250	87
4	0.2	60	10	25	63
		150	25	62.5	79
		300	50	125	117
		600	100	250	154
6	0.5	180	10	10	73
		450	25	25	79
		900	50	50	81
		1800	100	100	92
7	0.5	274	10	10	62
		685	25	25	65
		1370	50	50	70
		2740	100	100	62
Effluent	0.5	12	10	285	66
		30	25	712	43
		60	50	1425	52
		120	100	2850	62
DMSO	-	-	25	-	62

[a] 50 µL per plate.

[b] benzene extracts of NaOH-neutralized leachate and effluent water samples subsequently dissolved in DMSO for mutagenic testing.

Table 8. Mutagenic activity (strain TA98, plus S-9) of Clover Bar landfill leachates: summary.

Sample	Revertants per mg Extract	mg Extract per L H_2O	Total Revertants per L H_2O	BaP Required to give Equivalent Activity (µg/L)
	I/II[a]	I/II	I/II	I/II
1	38	33	1260	13.8
3	54/126	5.5/2.6	297/328	3.3/3.6
4	36/150	9.5/2.4	342/360	3.8/4.0
6[b]	44	5760/18	790	8.7
7[b]	0/4.4	3775/27	0/120	1.3
Effluent	110/0	0.38/0.042	40/0	0.44

[a] Series I and II represent benzene extracts of leachate and effluent water samples dissolved in DMSO for mutagenic testing; all samples from Series II were first neutralized with NaOH to pH 7.0 to prevent uptake of carboxylic acids into benzene.

[b] Leachates 6 and 7 were notably acidic.

This value was not reproducable in January for which the same amount of extract per plate showed no detectable mutagenic activity.

Activities of leachate and effluent water extracts were also expressed in terms of the amount of benzo(a)pyrene (BaP) required to give an equivalent activity per litre of water. This is a useful way of expressing these data since it allows for comparison of these activities between different preparations of S-9 and between different laboratories. Benzo(a)pyrene was chosen since it is representative of the class of compounds (i.e., polycyclic aromatic hydrocarbons) which were among the mutagenic compounds known to be present in the samples.

The mutagenic activities reported here are very low when compared with the findings of Pelon et al. (1977) for Mississippi River water at certain sites in Louisiana. They found activities without S-9 as high as 7850 and 8500 revertants per litre of water on strains TA100 and TA98, respectively. The method by which these activities were obtained differed from our approach. In their experiments, river water (2 mL) was directly incorporated into the agar overlay and dose per plate was adjusted by dilution of this volume

Recommendations for further elaboration of the mutagenic activity of leachate and effluent waters might include use of other strains (TA100 and TA1538) and tests without S-9. Pelon et al. (1977) found that water from the Mississippi River could induce reversion in all five of the principal Ames strains and activity was frequently present without activation enzymes. Direct testing of water as opposed to water extracts in DMSO may detect mutagenic compounds which are otherwise not removed by the organic extraction procedure. This remains to be proven.

5.13 POLYCHLORINATED BIPHENYLS

An extensive search for polychlorinated biphenyls (PCB's) in the leachates revealed the presence of only one PCB above detection limits of 0.003 µg/L. Total aroclor was seen and measured in Leachate 7

from the second series at a level of 0.08 µg/L. Other chlorinated hydrocarbons, including aldrin, heptachlor, DDE, DDD, DDT, mirex, HCB, chlordane, and o,p-DDT, were not found in these leachate extracts.

5.14 BASIC COMPOUNDS

Following initial extraction of the original leachates with benzene, an aqueous fraction containing basic compounds remained. No attempt was made to identify individual basic substances, but a quantitative measure of their contribution to the total organic carbon was made. Significant amounts of these materials appeared in extracts from four leachates in the first series of samples--Leachates 1 (2.6 mg/L), 2 (2.1 mg/L), 2A (1.8 mg/L), and 6 (2.2 mg/L). No basic compounds were observed in the remaining leachates. Basic components occur in the leachates in an apparently random pattern throughout the landfill site.

5.15 PRIORITY POLLUTANTS

The United States Environmental Protection Agency (EPA) has classified 129 toxic chemicals as priority pollutants (Keith and Telliard 1979; Finegar et al. 1979) in continuing, major studies to improve performance and pretreatment standards as well as analytical methodology for industrial wastewater effluents. It is only a small step from wastewater discharges to sanitary landfill disposal of hazardous materials. Among the priority pollutants are hydrocarbons (such as ethyl benzene), some are halogenated hydrocarbons (e.g., hexachloro-butadiene), plasticizers (di-n-octyl phthalate), nitrogen-containing compounds such as nitrobenzene, phenolic compounds like dimethyl phenol, pesticides, 13 trace metals, and cyanides.
A concerted effort to identify and measure priority pollutants was not made in this study; however, mass spectral data in the present study revealed several members in the EPA classification in Leachate 7. Priority pollutants identified in the entire study were dichlorophenol, dimethyl phenol, phenol, naphthalene, chlorophenol, and one poly-chlorinated biphenyl.

A listing of all organic parameters identified in this study is reported in Table 9. These include the general parameters as well as the most important individual compounds as members of groups such as alkanes, aromatics, organic acids, and phenols.

In a closely related study, James F. MacLaren Consultants in Edmonton are conducting an investigation of landfill leachates in the BACM site and at the same time are carrying out a literature survey of work on related subjects. Throughout our project, and that of the MacLaren Group, the two groups have been in close contact.

The conference on "Benefitting from Environmental Monitoring" held in Arlington, VA on 29 and 30 October 1979 was attended by Bruce Baker. His report on that conference was submitted with the draft final report of this project on 6 March 1980. This document is submitted as the final report of the project "Chemical Composition and Mutagenicity of Clover Bar Landfill Leachates" as required in the terms of reference for the study noted above.

Table 9. Organic compounds identified in leachates.

Gross Parameters:

Total Organic Carbon
Suspended Solids
Chemical Oxygen Demand
pH

Classes of Compounds:

Tannins and Lignins
Phenols
Carbohydrates
Alkane Hydrocarbons
Aromatic Hydrocarbons
Polar Compounds
Organic Acids
Organic Sulphur Compounds
Bases

Individual Compounds:

Alkanes

n-hexadecane C_{16}
n-heptadecane
n-octadecane
n-nonadecane
n-eicosane C_{20}
n-heneicosane
n-docosane
n-tricosane
n-tetracosane C_{24}
n-pentacosane C_{25}
n-hexacosane
n-heptacosane
n-octacosane
n-nonacosane
n-triacontane C_{30}
n-henatriacontane
n-doatriacontane
n-tritriacontane C_{33}
n-tetratriacontane C_{34}
n-pentatriacontane
n-hexatriacontane
n-heptatricontane
n-octatricontane
n-nonatriacontane
n-tetracontane C_{40}

Aromatics

naphthalene, dimethyl naphthalene (2 isomers)

Organic Acids

butyric, valeric, hexanoic, cyclohexane carboxylic, heptanoic, octanoic, nonanoic, decanoic, benzene acetic, benzene propionic, valeric acid methyl methyl ester.

Phenols

phenol, chlorophenol, methyl phenol (4 isomers), ethyl or dimethyl phenol (5 isomers), dichlorophenol (3 isomers)

Priority Pollutants

dichlorophenol
dimethyl phenol (xylenol)
polychlorinated biphenyls
phenol, naphthalene
chlorophenol, dichlorophenol

6. SUMMARY

Leachates from the Clover Bar landfill site contain variable amounts of dissolved organic compounds as indicated by the total organic carbon values varying from 40 to 16 000 mg/L. A general distribution of increasing TOC values from west to east across the site was found, with leachate from Wells 3 and 4 having the lowest TOC values and leachates from Wells 2, 6, and 7 containing the highest TOC levels. A corresponding distribution was found in pH with Wells 3 and 4 containing slightly alkaline leachates and Wells 2, 6, and 7 slightly acidic leachates. This trend is probably related to the generation of water-soluble organic acids by microbial decomposition of waste materials. The TOC content of the effluent samples was low, only 8 mg/L, reflecting only limited contact between leachates and groundwater.

Chemical oxygen demands of leachates showed the same west-to-east trend over a range from 300 to 30 000 mg/L. In the case of samples with high TOC (between 7000 and 16 000 mg/L), the COD was much greater--18 000 to 30 000 mg/L, reflecting the presence of interfering inorganic ions and elevated reducing conditions in the eastern part of the site.

The major compounds identified were organic acids which account for about 25% of the total organic carbon in Wells 2, 6, and 7. Straight chain acids, butyric to decanoic (C_4 to C_{10}), were identified together with benzene acetic acid, benzene propionic acid, and cyclohexane carboxylic acid. These acids are products of microbial activity and have previously been found in landfill sites in Europe and the United States. Lower molecular weight acids, acetic and propionic, were probably lost in sampling and extraction and were therefore not found in this study. They may account for a major part of the TOC in Clover Bar leachates.

Much smaller amounts of tannins and lignins, alkane hydrocarbons, organic sulphur compounds, elemental sulphur, phenols, carbohydrates, and polycyclic aromatic hydrocarbons were found.

Tannins and lignins ranged from 3 to 2200 mg/L following the same pattern in the landfill site as TOC and organic acids. In the effluent, they amounted to 1 mg/L and were very similar to levels seen

in surface waters. Aliphatic hydrocarbons ranged from 0.3 to 6.5 mg/L but did not follow the gradation shown by other components. The carbon preference index of these hydrocarbons is consistent with that of waste crude oil and microbial activity. Both organic sulphur compounds and elemental sulphur were found. Sulphur-containing organic compounds followed the west-to-east distribution previously noted. Elemental sulphur showed the opposite trend. Samples with high organic sulphur (2.9 to 9.7 mg/L) displayed less than 1 µg/L elemental sulphur, whereas a sample with 2.8 mg/L elemental sulphur contained only 0.09 mg/L organic sulphur compounds. Phenols were measured colorimetrically and identified by gas chromatography-mass spectrometry. Concentrations ranged from 0.03 to 7.60 mg/L in the leachates with less than 1 µg/L in the effluent. Phenolic compounds identified were phenol, four methyl phenol isomers, five isomers of ethyl or dimethyl phenol, chlorophenol, and three isomers of dichlorophenol. These compounds are common in oil refinery and chemical manufacturing wastes and are all on the United States list of "priority pollutants". Of the compounds found in the leachate samples, the phenols are among the most toxic. Polychlorinated biphenyls were found low in concentrations (0.08 g/L, in one sample). Carbohydrates were measured in a range from 4 to almost 600 µg/L, with highest levels in leachates characterized by high TOC--a similar pattern to the majority of parameters measured in this study. Polyaromatic hydrocarbons, including priority pollutants fluoranthene, benzanthracenes, benzopyrenes, benzofluoranthenes, chrysenes, and dibenzanthracenes, were either absent or present in very small quantities, totalling less than 1 µg/L.

Difficulties in the chemical analyses of leachates were experienced. Losses occurred from the high volatility of low molecular weight components. A supplementary approach in which volatile organic materials are purged from the sample, trapped, and analyzed may have revealed the presence of other "priority pollutants". Such new approaches could be profitably incorporated into an analytical procedure for the characterization of sanitary landfill leachates.

The Ames test showed mutagenic activity in extracts of the leachate samples and in the first effluent sample. The activity was not high, ranging from the equivalent of 0.4 µg of benzo(a)pyrene per litre of effluent to the equivalent of 13.8 µg/L of benzo(a)pyrene in Leachate 1 extracted under acidic conditions. In this study, organic materials were extracted from the leachate samples for testing.

7. RECOMMENDATIONS

It is recommended:

1. That a standard methodology be adopted for the chemical analysis of landfill leachates, the method of analysis to be based on the United States Environmental Protection Agency publication "Sampling and Analysis Procedures for Survey of Industrial Effluents for Priority Pollutants", with appropriate modifications. The modifications should include separation of the acidic and phenolic components prior to analysis for the measurement of low molecular weight acids. A supplementary system in which volatile organic materials are purged from the sample, trapped, and analyzed is also recommended for measurement of low molecular weight pollutants, particularly for organic acids. All components should be analyzed by gas chromatography-mass spectrometry because gas chromatography alone can lead to ambiguous results.
2. That a standard methodology be adopted for biological testing of landfill leachates for mutagenicity by the Ames test. This method should consist of: (a) direct incorporation of the filtered leachate sample into the agar used in the Ames test to minimize loss of volatile components; and (b) testing of the "base-neutral" and "acid" extracts of the leachates on at least four *Salmonella* strains in order to detect a wide range of possible mutagenic compounds.
3. That these methods be used to monitor leachates from Clover Bar and other landfill sites in Alberta with special attention to sites containing industrial and hazardous wastes.

4. That processes which alter the composition of wastes in the Clover Bar and other Alberta landfill sites, leading to the release of dissolved organic matter, be investigated--objective being to control existing releases and to aid in the design of future sites. The investigation should include chemical, microbiological, hydrological, and engineering components.

8. REFERENCES CITED

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